

Article

Fate of Octyl- and Nonylphenol Ethoxylates and Some Carboxylated Derivatives in Three American Wastewater Treatment Plants

Jorge E. Loyo-Rosales, Clifford P. Rice, and Alba Torrents

Environ. Sci. Technol., **2007**, 41 (19), 6815-6821 • DOI: 10.1021/es070713i • Publication Date (Web): 05 September 2007

Downloaded from <http://pubs.acs.org> on March 18, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Fate of Octyl- and Nonylphenol Ethoxylates and Some Carboxylated Derivatives in Three American Wastewater Treatment Plants

JORGE E. LOYO-ROSALES,^{†,§}
CLIFFORD P. RICE,[‡] AND
ALBA TORRENTS^{*,†}

Environmental Engineering Program, Department of Civil and Environmental Engineering, University of Maryland, College Park, Maryland 20742 and Environmental Management and Byproducts Utilization Laboratory, ANRI, ARS/USDA, 10300 Baltimore Avenue, Beltsville, Maryland 20705

The fate of a comprehensive group of nonylphenol and octylphenol ethoxylates (APEOs) and several of their carboxylated derivatives was studied in three American wastewater treatment plants (WWTPs), two of which included advanced treatment. Influent and effluent concentrations of the alkylphenolic compounds (APEs) in the three plants were very similar, but effluent concentrations showed a seasonal dependency: both carboxylate and ethoxylate concentrations in the effluents were higher in winter than in summer. Sorption to particulate matter was higher for nonylphenolic compounds than for their octylphenolic counterparts, in agreement with their difference in K_{ow} values. Both effluent concentrations and the removal efficiency of the APEOs were strongly correlated to water temperature, but no correlation was found with suspended solids or organic carbon removal. Although APEO removal from wastewater was high, overall removal from the WWTPs, including APEOs in waste sludge and transformation products, was relatively low and suggested that advanced treatment does not invariably result in better APEO removal. Additionally, a survey of urban sewers suggested that household products still constitute an important source of the APEOs reaching WWTPs.

Introduction

Alkylphenol ethoxylates (APEOs), a widely used family of surfactants composed mainly of nonylphenol and octylphenol ethoxylates (NPEOs and OPEOs, respectively), undergo a rapid transformation in wastewater treatment plants (WWTPs) into short-chain APEOs, the parent alkylphenols (APs, octylphenol, OP or OP0EO, and nonylphenol, NP or NP0EO), and carboxylated derivatives, which include the alkylphenoxyethoxy carboxylates (APECs), and the carboxy-alkylphenoxyethoxy carboxylates (CAPECs) (1, 2). Several of the transformation products are of toxicological concern due

to their estrogenic properties (3), and they have been linked to endocrine-disruption effects in biota exposed to WWTP effluents (e.g., refs 4, 5).

It has been argued that American WWTPs are more effective than their European counterparts at removing APEOs (6). However, the fate of APEO-related compounds (APEs) in WWTPs has been extensively studied in Europe (e.g., ref 1), but not in the United States (7). Except for ref 8, most American studies focus on APE concentrations in effluents and receiving waters (e.g., ref 9), and/or limit the number of analytes to the more toxicologically relevant transformation products—NP, the low molecular weight ethoxymers (nonylphenol monoethoxylate, NP1EO, and nonylphenol diethoxylate, NP2EO), and the carboxylated derivatives nonylphenoxycetic acid (NP1EC), and nonylphenoxyethoxycetic acid (NP2EC)—while excluding the long-chain parent compounds (10–12). It is the latter, however, that reach the WWTPs in the influent wastewater, and the analysis of as many of the APEs as possible is necessary to construct mass balances. Additionally, few studies have addressed APEO degradation in advanced treatment systems, and these studies have only included a few of the APEs (e.g., ref 13).

This work describes the fate of a comprehensive set of APEs in three American WWTPs, two of which had advanced treatment (Table 1). NP1-16EO, OP1-5EO, NP, OP, and their carboxylated derivatives NP1EC, NP2EC, and OP1EC were analyzed quantitatively, whereas NP3EC and NP4EC were monitored qualitatively. Seasonal changes in the concentrations and removal efficiencies of these compounds from wastewater and their overall elimination from the WWTPs are also discussed.

Experimental Section

Standards and Reagents. Standards for NP (Schenectady International, Schenectady, NY; purity $\geq 95\%$), OP (Aldrich, Milwaukee, WI; 97%), NP2EO (R&D product from Aldrich), NP1EC (R&D product, Huntsman Chemicals, Austin, TX), NP2EC (Aldrich; 90%), and OP1EC (R&D product, Huntsman) were used as provided. NP1EO, NP3EO, NP4EO, NP5EO, and OP1-5EO were purified in the laboratory as described previously (14, 15) (purity $\geq 99\%$, except for OP1EO, 94%). A commercial mixture (Surfonic N-95, Schenectady International; $>97\%$; characterized by Huntsman, Table S1) was used as standard for NP6-16EO. $^{13}\text{C}_6$ -substituted standards for isotope-dilution mass spectrometry (IDMS) were synthesized by Ferguson et al. (16), except for $^{13}\text{C}_6$ -NP (Cambridge Isotope Laboratories Inc., Andover, MA). Solvents were high purity, pesticide grade from Burdick & Jackson (Honeywell International Inc., Muskegon, MI). Carbon-free deionized water (DI water) was obtained from a NANOpure system (Barnstead International, Dubuque, IA).

Site Descriptions and Sampling Procedures. Grab wastewater and sludge samples were obtained in 2004 and 2005 from three large American WWTPs (Table 1). Samples were labeled as “summer” if water temperature was $\geq 20^\circ\text{C}$ and as “winter” if it was $\leq 15^\circ\text{C}$. All liquid samples were collected in previously baked amber glass containers, and transported in ice to the laboratory. Sludge was frozen at -20°C upon arrival, whereas water samples were filtered as described in ref 17; the filters were air-dried and weighed to calculate suspended solids, and extracted to evaluate their APEO content. Two sampling events were conducted in sewers from the Chicago, IL, area to better understand APEO sources. The first took place in March 2005 and included five raw sewage samples: two originating mainly from residential

* Corresponding author phone: +1-301-405-1979; fax: +1-301-405-6707; e-mail: alba@eng.umd.edu.

[†] University of Maryland.

[‡] Environmental Management and Byproducts Utilization Laboratory.

[§] Current address: Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720.

TABLE 1. Wastewater Treatment Plant Characteristics and Sampling Events

name	plant 1	plant 2	plant 3
location	mid-atlantic	mid-atlantic	midwest
capacity, mgd	180	370	350
population served, mi	1.3	2.0	1.0
treatment (after primary)	modified Ludzack–Ettinger	activated sludge + separate stage nitrification/denitrification	nitrifying activated sludge
final chlorination	yes	yes	no
time in biological treatment, hrs ^a	5–10	~6	6–14
sludge retention time, days	7–13	secondary sludge: 1–1.5 nitrification sludge: 14–20	7–12
samples obtained			
	raw influent	raw influent	primary influent
water	primary effluent	primary effluent	primary effluent
	secondary effluent	secondary effluent	aeration tank effluent
	final effluent	tertiary effluent	final effluent
		final effluent	
sludge	primary	primary	primary
	secondary	secondary	prim + secondary
		tertiary	
sampling events	Sep 2004 (24.5)	Jul 2004 (25.2)	Mar 2005 (9.3) ^b
(in situ average water <i>T</i> , °C)	Oct 2004 (20.5)	Aug 2004 (25.7)	Aug 2005 (23.5) ^b
	Feb 2005 (13.8)	Feb 2005 (14.4)	
	Mar 2005 (14.0) ^b	Mar 2005 (14.0) ^b	

^a This is the hydraulic residence time (HRT) in activated sludge reactors in plants 1 and 3; but in plant 2 it is the total HRT in the secondary, nitrification and denitrification reactors. ^b Collected sludge samples.

zones, one from a commercial area, one from an industrial area, and one was the influent to plant 3. The second sampling event occurred in August 2005 and consisted of 5 24 h composite raw sewage samples collected in residential areas.

Extraction and Analysis. NP0-16EO, OP0-5EO, NP1-2EC, and OP1EC were analyzed quantitatively, and NP3-4EC qualitatively, in the dissolved fraction of the wastewater samples. Particulate matter and sludge were analyzed for the APEOs, but not the APECs. Extraction methods for the different matrices and analytes were published elsewhere (15, 17), and consisted of solid-phase extraction (SPE) using hyper-cross-linked hydroxylated poly(styrene-divinylbenzene) copolymer cartridges for the APEOs in wastewater; liquid–liquid extraction with dichloromethane for the APECs; Soxhlet extraction with methanol for the APEOs in particulate matter; and for sludge, accelerated solvent extraction with hexane and acetone, followed by SPE cleanup with amino-propyl silica cartridges. Extracts were analyzed by electrospray LC-MS-MS using a mixed-mode column (size-exclusion and reversed-phase adsorption) for separation. Detection was done in multiple-reaction monitoring mode using electrospray positive for the APEOs and electrospray negative for the APs and APECs. An isotope-dilution mass spectrometry approach was used for quantitation, except for the APECs, which were quantitated by external standard (17). NP3EC and NP4EC were measured qualitatively in the same LC-MS-MS runs as the rest of the APECs; ion transitions monitored were 365.4 > 219.0 *m/z* for NP3EC, and 409.4 > 219.0 for NP4EC; cone voltages were 35 and 40 V, respectively, and collision energy was 25 eV for both compounds.

Results and Discussion

APE Concentrations in WWTP Influent and Effluents.

Although the WWTPs are located in different metropolitan areas, total APE concentrations in the WWTP influents were remarkably similar; relatively small variations were observed between plants and between seasons (Table 2, Figure 1A and B). The similitude in total APE concentrations in the influents might be due to the large amounts of wastewater treated by the WWTPs, the size of the populations served (Table 1), and the widespread use of APEOs. These concentrations were comparable to those observed elsewhere (1, 18). In the

influent, there were seasonal differences in the particular case of the NPEOs oligomer distribution: short-chain NPEO molar concentrations (NP0-3EO) represented 42% of the total in the summer, but only 23% in winter. This difference might be due to a higher microbial transformation rate of the long-chain NPEOs (NP4-16EO) into the short-chain NPEOs during transit to the WWTPs, induced by higher water temperatures in the summer.

APE concentrations in the final effluents from the three plants were also similar in spite of the different treatment processes. However, in contrast to the influents, there was a seasonal effect on APE concentrations in the effluents (Table 2, Figure C and D); total NPEO and OPEO concentrations were more than 7 times higher in winter than in summer, and the APECs were 5 times higher in winter (Table 2). Compared to previous reports, APE concentrations in the effluents tended to be in the lower end (1, 18–20); presumably due to the use of advanced treatment, because most of the plants reported in the literature are limited to secondary or even primary treatment.

As expected for microbial-mediated transformations, the seasonal differences in total APE concentrations in the effluents appear to be related to temperature. NPEO, OPEO, and APEC effluent concentrations in the summer ($T \geq 20$ °C) were significantly different from the respective concentrations in winter ($T \leq 15$ °C) (Mann–Whitney test, $P \leq 0.01$, 21). Other variables, such as APE concentrations in the influents, were not correlated to effluent concentrations. Seasonal differences in effluent concentrations were especially pronounced for the long-chain NPEOs; average NP4-16EO concentrations were more than 15 times higher in winter than in summer. In contrast, NP0-3EO concentrations were only 7 times higher in winter (Table 2). At the same time, the ratio of NP0-3EO to NP4-16EO decreased from 10 in summer to 4 in winter, suggesting that temperature has a greater effect on the de-ethoxylation rate of the long-chain NPEOs than the degradation rate of the short-chain EOs.

APEO Removal Efficiency from Wastewater. When samples from the same season are compared, APEO removal is equally comparable across the three studied WWTPs. Average NP0-16EO removal was 99.1% (SD = 0.28) in summer; significantly different (*t* test, $\alpha = 0.05$) from winter, 93.7%

TABLE 2. Total APEO (Dissolved + Particulate Matter) and Dissolved APEC Concentrations in WWTP Influent and Effluents^a

					concentration, $\mu\text{g/L}$				
			plant	$T, ^\circ\text{C}$	NP0-3EO ^b	NP4-16EO ^c	NP0-16EO	OP0-5EO	APEC ^d
influent	summer	Sep 04	1	23.9	262	499	760	6.57	0.28
		Oct 04	1	20.3	128	545	672	7.32	1.04
		July 04	2	25.7	82.3	587	670	4.70	1.48
		Aug 04	2	25.8	160	265	425	6.82	3.23
		mean (SD)		23.9	158 (76)	474 (144)	632 (144)	6.36 (1.14)	1.50 (1.25)
	winter	Feb 05	1	15.0	149	745	894	7.14	1.68
		Mar 05	1	14.0	47.6	474	521	5.75	0.80
		Feb 05	2	14.0	127	722	849	8.25	1.31
		Mar 05	2	14.0	68.5	638	707	6.00	1.28
		Mar 05	3	9.9	50.2	610	660	5.13	2.65
effluent	summer	Sep 04	1	24.8	3.48	0.338	3.82	0.548	7.46
		Oct 04	1	20.8	3.92	0.272	4.19	0.215	18.7
		July 04	2	24.7	4.42	0.329	4.75	0.239	24.3
		Aug 04	2	25.6	1.58	0.042	1.62	0.005	25.9
		Aug 05	3	23.5	2.53	0.690	3.22	0.039	7.58
		mean (SD)		23.9	3.19 (1.14)	0.334 (0.232)	3.52 (1.20)	0.21 (0.22)	16.8 (8.9)
	winter	Feb 05	1	14.0	32.3	5.97	38.2	2.08	121
		Mar 05	1	14.0	17.6	5.39	23.0	1.62	99.3
		Feb 05	2	15.0	20.7	8.42	29.1	1.54	57.6
		Mar 05	2	14.0	15.9	1.28	17.2	0.84	79.7
		Mar 05	3	9.3	21.5	5.08	26.6	1.82	49.9
		mean (SD)		13.3	21.6 (6.4)	5.22 (2.57)	26.8 (7.8)	1.58 (0.47)	81.5 (29.3)

^a Individual concentrations for NP0-5EO, OP0-5EO, and the APECs are available in the Supporting Information section (Table S3). ^b NP0-3EO = short-chain NPEOs. ^c NP4-16EO = long-chain NPEOs. ^d APEC includes NP1-2EC and OP1EC.

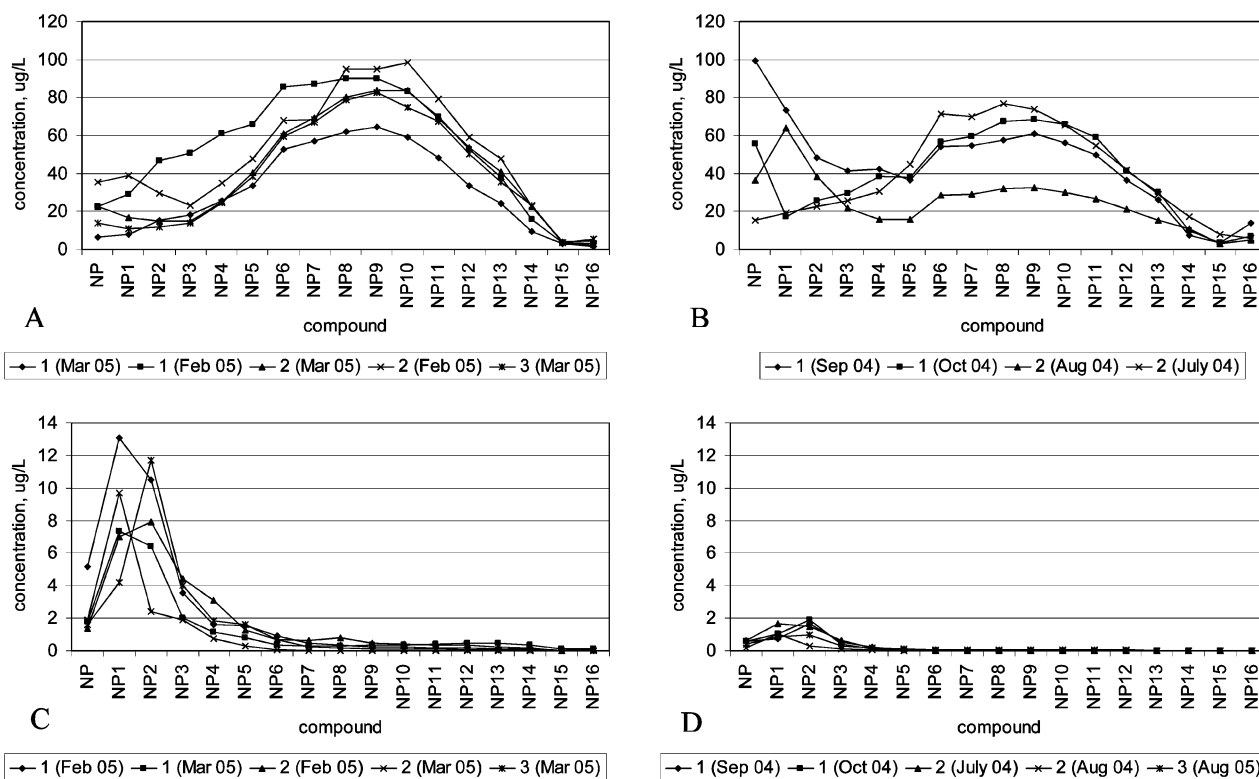


FIGURE 1. Total NPEO concentrations (dissolved + particulate matter) in influent wastewater in winter (A) and summer (B); and in final effluents in winter (C) and summer (D) for WWTPs 1, 2, and 3 (sampling dates in parentheses).

(SD = 1.2). OP0-5EO removal also showed statistically significant differences between summer, 96.6 (3.4)%, and winter, 71.5 (10.5)%. NPEO removal was significantly higher in these three WWTPs than the average reported by Ahel et al. (1), 59% (SD = 18), in 11 Swiss WWTPs with activated-sludge treatment.

As expected (1), APECs were formed in the three WWTPs. APEC accumulation showed a larger variation than APEO degradation between WWTPs, but there were also statistically

significant differences (t test, $\alpha = 0.05$) between summer and winter. Including APEC concentrations in removal calculations decreased removal efficiencies, especially in winter; e.g., NP0-16EO removal efficiency in winter decreased from 93.7 to 75% when NP1-2EC were included. Removal efficiencies would be even lower if the concentrations of NP3-4EC were considered. Both compounds were formed in the three WWTPs, generally at lower but still significant concentrations compared to NP1-2EC (Figure S1).

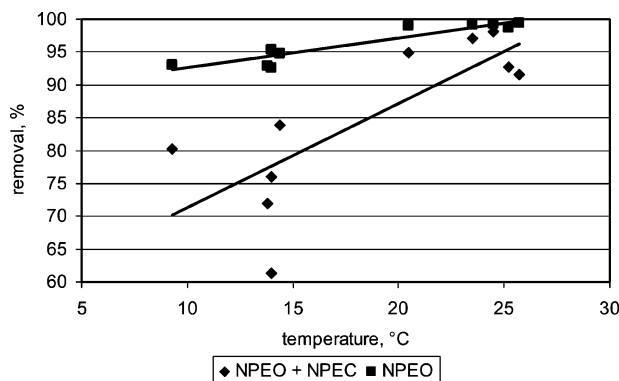


FIGURE 2. NP0-16EO (squares) and NP0-16EO + NP1-2EC (diamonds) removal from three WWTPs as a function of temperature.

It has been suggested that APEO removal from WWTPs is correlated to WWTP performance (1), including organic carbon removal (22). The data obtained for this study do not support this suggestion; no correlation was found between APEO removal and total suspended solids (TSS), total organic carbon (TOC) or dissolved organic carbon removal (DOC) (Table S2). In fact, differences between summer and winter were small for the three parameters, and they were not statistically significant for TSS and DOC (t test, $\alpha = 0.05$), which should be expected because the WWTPs control these parameters. However, APEO removal was strongly correlated with temperature, $r^2 = 0.8689$, $p < 0.0001$ for NP0-16EO removal, $r^2 = 0.8787$, $p < 0.0001$ for NP0-5EO, and $r^2 = 0.7900$,

TABLE 3. NPEO/OPEO Concentration Ratios in Suspended Solids: Expected from $\log K_{ow}$ Values, and Measured from NPEO and OPEO Concentrations in Dissolved Phase and Suspended Solids

	$\log K_{ow}$ (24)				
	AP	AP1EO	AP2EO	AP3EO	AP4EO
NP	4.48	4.17	4.21	4.20	4.30
OP	4.12	4.10	4.00	3.90	3.90
NPEO/OPEO ratios in solids					
expected ^a	2.3	1.2	1.6	2.0	2.5
measured ^b					
mean	2.1	2.2	2.6	2.1	1.8
SD	1.4	1.2	1.2	1.0	0.7
n	34	30	40	38	29

^a From $10^{\log K_{ow,NPEO} - \log K_{ow,OPEO}}$ ^b From $([NPEO]_{part}/[NPEO]_{dissolved})/([OPEO]_{part}/[OPEO]_{dissolved})$.

$p = 0.0006$ for OP0-5EO. Including NP1-2EC concentrations to NP0-16EO removal decreases the strength of the correlation (Figure 2), $r^2 = 0.6004$, $p = 0.0084$, due to the higher variability in APEC accumulation between WWTPs. In spite of the variability, the inclusion of transformation products—NPECs in this case—provides a more complete representation of NPEO removal. As noted above, these removal values would be lower if other transformation products were included that were not quantified (NP3-4EC) or even analyzed (e.g., CAPECs).

APEO removal can also be affected by other factors, such as hydraulic and sludge residence times (HRT and SRT) (23). In this study, the three WWTPs sampled operated with similar

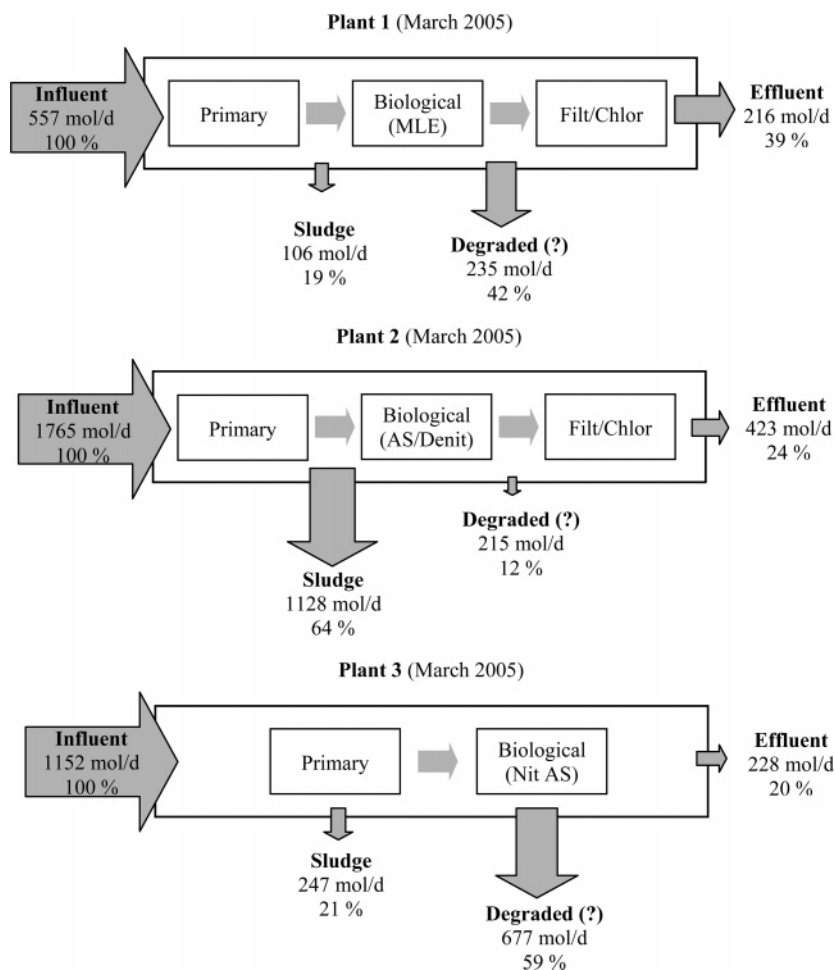


FIGURE 3. NPE (including NP0-16EO and NP1-2EC) mass balance in three WWTPs. Influent: total mass in influent (except for plant 3 in August, where it corresponds to the primary effluent); Sludge: total mass in waste primary and secondary sludge (plant 2 includes tertiary sludge); Effluent: total mass in final effluent; Degraded: estimated from influent - (sludge + effluent).

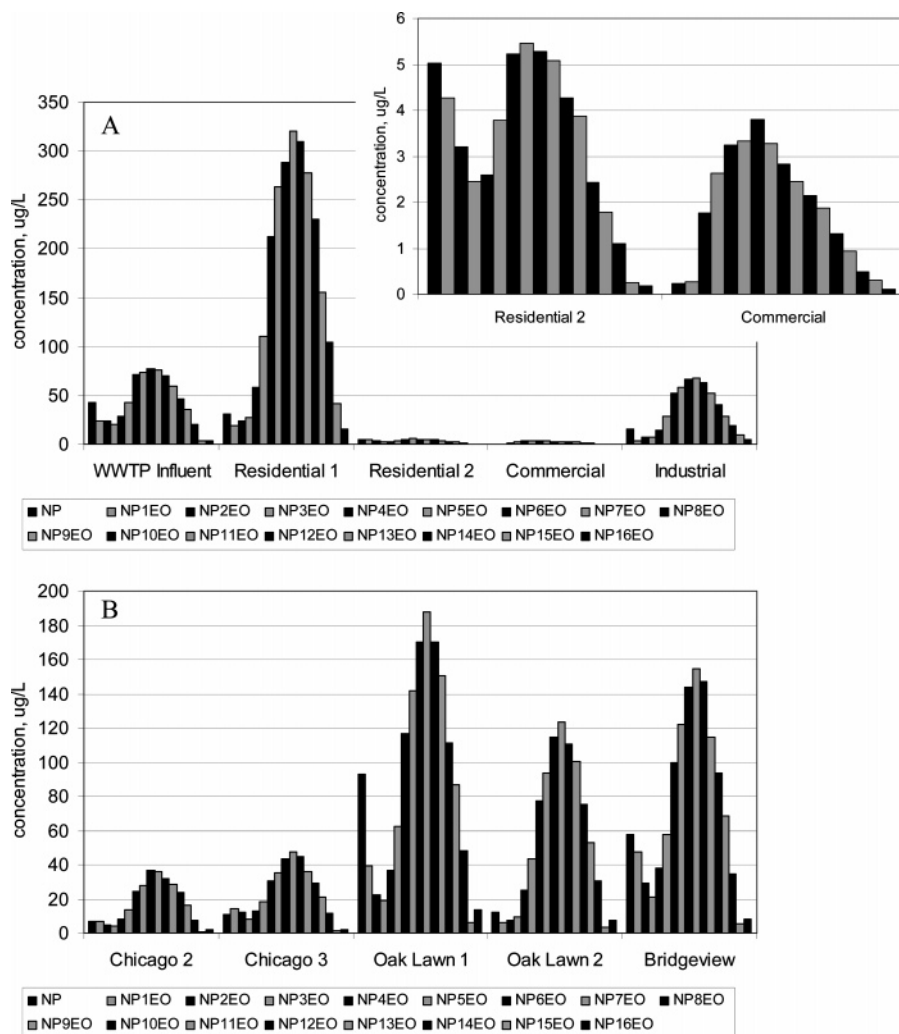


FIGURE 4. Total NP0-16EO concentrations (dissolved + particulate matter) in (A) grab sewage samples from commercial, industrial and residential areas in Chicago, IL, and (B) 24-h composite sewage samples from different residential areas in Chicago.

HRTs (Table 1); but plant 2 had a short SRT for its secondary sludge. APEO removal efficiencies in the secondary treatment stage of plant 2 (as low as 18%, data not shown) were much lower than in plant 3, suggesting that the higher efficiencies in plant 3 were a consequence of higher SRTs. The overall APEO removal efficiency for plant 2 would have remained high because of the significantly long SRT in its nitrification/denitrification step; nitrifying conditions have been also correlated with high APEO degradation (1).

Preferential Elimination of NPEOs vs OPEOs. Total average OP0-5EO concentrations in the influents were 35 times lower than NP0-5EO in summer and 26 times lower in winter (data in Table S3); but these ratios decreased to 16 and 15 respectively in the final effluents. At the same time, elimination efficiencies were higher for NP0-5EO, 82.1 (SD = 5.2) %, and significantly different (t test, $\alpha = 0.05$) to the OPEOs in winter, 71.5 (10.5)%, when biodegradation rates can be expected to be lower than in summer. These observations suggest preferential elimination of the NPEOs in the WWTPs, and a possible cause is the NPEOs higher affinity for solids. Both NPEOs and OPEOs partition to the organic matter in suspended solids because of their relative hydrophobicity ($\log K_{ow} \sim 4$, Table 3), but when comparing dissolved *versus* particulate bound concentrations, the NPEOs tended to be in higher proportions in the particulate matter. Using the $\log K_{ow}$ values, the expected NPEO to OPEO ratios in the suspended solids are between 1.2 and 2.5 (Table 3). The ratios calculated from the APEO concentrations mea-

sured in the suspended solids from the WWTPs fell in a similar range, 1.8–2.6 (Table 3); suggesting that a higher proportion of the NPEOs compared to the OPEOs could have been eliminated with the waste sludge.

Overall APE Removal from WWTPs. Due to the affinity of the short-chain APEOs to solids, a complete assessment of APE removal in WWTPs cannot be performed without considering the APEOs leaving the plant with the sludge. Most studies only report elimination from wastewater, not accounting for APEO elimination in sludge (8). In the present study, sludge and water concentrations were used to estimate overall APE removal (Figure 3) and compare it to Ahel and collaborators' study of two Swiss WWTPs (1), where at least 60–65% of the NPEOs entering these plants were discharged into the environment, mostly in the form of degradation products. Our results varied widely: plant 1 performed similarly to the Swiss plants; almost 60% of the incoming APEO mass was released in the effluent and sludge, leaving approximately 40% available for microbial transformation (this value was obtained by difference and might include losses through processes other than biotransformation, such as volatilization). Plant 3 released a smaller amount; slightly more than 40% in the winter, and around 30% in the summer. In the case of plant 2, most of the APEO elimination occurred in the solids, resulting in almost 90% of the APEOs being released from the WWTP. This might be due to the shorter SRT causing a higher production and elimination of sludge. Presumably, the short-chain APEOs formed during secondary

treatment would attach to the solids and leave the plant before microbial degradation can occur. An accurate evaluation of these phenomena would require the analysis of a more comprehensive set of the APEO biotransformation products, such as long-chain APECs and CAPECs, which could increase the amounts of APEO-related compounds released from the plant. Additionally, to obtain truly representative mass balances, composite samples would be necessary to account for the fact that the solids remain in the WWTPs for several days and they are exposed to wastewater with varying concentrations of the APEs over this period of time. In any case, these results suggest that WWTPs with advanced treatment might not necessarily improve overall APE removal, even if removal efficiency from wastewater is high.

APEO Sources. A survey of sewage samples from different areas in Chicago showed that NPEO concentrations and individual oligomer distributions in residential samples were comparable to industrial and commercial sources, as well as to the WWTP influent (Figure 4A); furthermore, NPEO concentrations in one of the residential samples were significantly higher than in the other sites. A more detailed survey of sewers in different residential areas of Chicago supported these observations (Figure 4B). Although flow rates were not measured and the actual contribution of each type of sewage to the total loading of the WWTP could not be computed, these results suggest that residential areas might still be important sources of NPEOs to WWTPs. This observation was somewhat unexpected because it is implied in the literature that household applications of the APEOs are relatively insignificant compared to other uses, accounting for only 15% of the total (25), maybe because they were reportedly substituted in household products with alcohol ethoxylates since the mid-1970s (26). Additionally, the U.S. EPA instituted a program for the voluntary phase out of NPEO use and manufacture, and the major American laundry detergents are free of NPEOs (27) although some detergents still contain them (28). The OPEOs detected in this survey followed similar patterns to the NPEOs, but their concentrations did not vary proportionally to NPEO concentration, suggesting different sources for these two families of compounds even within residential sewers.

Acknowledgments

This work was partially funded by the Maryland Water Resources Research Council (WRRC) and the U.S. Geological Survey in Boulder, CO. J.E. Loyo-Rosales was recipient of a Conacyt-Fulbright/Garcia-Robles scholarship. We also wish to acknowledge the assistance from Larry Barber, Thomas Granato, Hyunook Kim, Richard Lanyon, John Martin, Todd Nettesheim, Mark Ramirez, the U.S. EPA Region V, and the WWTPs' personnel in obtaining the samples and/or for their valuable comments on this article.

Supporting Information Available

Composition of the commercial mixture used as NP6-16EO standard; TSS, TOC, and DOC removal in the WWTPs; individual concentrations for the short-chain APEOs and APECs in WWTP influents and effluents; and NP1-2EC versus NP3-4EC formation in two of the plants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Ahel, M.; Giger, W.; Koch, M. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—I. Occurrence and transformation in sewage treatment. *Water Res.* **1994**, *28* (5), 1131–1142.
- Ding, W.-H.; Fujita, Y.; Aeschmann, R.; Reinhard, M. Identification of organic residues in tertiary effluents by GC/EI-MS, GC/CI-MS, and GC/TSQ-MS. *Fresenius J. Anal. Chem.* **1996**, *354* (1), 48–55.
- Jobling, S.; Sumpter, J. P. Detergent components in sewage effluent are weakly oestrogenic to fish: An in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes. *Aquat. Toxicol.* **1993**, *27* (3–4), 361–372.
- Lye, C. M.; Frid, C. L. J.; Gill, M. E.; Cooper, D. W.; Jones, D. M. Estrogenic alkylphenols in fish tissues, sediments, and waters from the U.K. Tyne and Tees estuaries. *Environ. Sci. Technol.* **1999**, *33* (7), 1009–1014.
- Solé, M.; López de Alda, M. J.; Castillo, M.; Porte, C.; Ladegaard-Pedersen, K.; Barceló, D. Estrogenicity determination in sewage treatment plants and surface waters from the Catalanian area (NE Spain). *Environ. Sci. Technol.* **2000**, *34* (24), 5076–5083.
- Renner, R. European bans on surfactant trigger transatlantic debate. *Environ. Sci. Technol.* **1997**, *31* (7), 316A–320A.
- Maguire, R. J. Review of the persistence of nonylphenol and nonylphenol ethoxylates in aquatic environments. *Water Qual. Res. J. Can.* **1999**, *34* (1), 37–78.
- Kubeck, E.; Naylor, C. G. Trace analysis of alkylphenol ethoxylates. *J. Am. Oil Chem. Soc.* **1990**, *67* (6), 400–405.
- Snyder, S. A.; Keith, T. L.; Verbrugge, D. A.; Snyder, E. M.; Gross, T. S.; Kannan, K.; Giesy, J. P. Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. *Environ. Sci. Technol.* **1999**, *33* (16), 2814–2820.
- Field, J. A.; Reed, R. L. Nonylphenol polyethoxy carboxylate metabolites of nonionic surfactants in U.S. paper mill effluents, municipal sewage treatment plant effluents, and river waters. *Environ. Sci. Technol.* **1996**, *30* (12), 3544–3550.
- Rudel, R. A.; Melly, S. J.; Geno, P. W.; Sun, G.; Brody, J. G. Identification of alkylphenols and other estrogenic phenolic compounds in wastewater, septage, and groundwater on Cape Cod, Massachusetts. *Environ. Sci. Technol.* **1998**, *32* (7), 861–869.
- Hale, R. C.; Smith, C. L.; de Fur, P. O.; Harvey, E.; Bush, E. O.; La Guardia, M. J.; Vadas, G. G. Nonylphenols in sediments and effluents associated with diverse wastewater outfalls. *Environ. Toxicol. Chem.* **2000**, *19* (4), 946–952.
- Bennie, D. T.; Sullivan, C. A.; Lee, H.-B.; Maguire, R. J. Alkylphenol polyethoxylate metabolites in Canadian sewage treatment plant waste streams. *Water Qual. Res. J. Can.* **1998**, *33* (2), 231–252.
- Datta, S.; Loyo-Rosales, J. E.; Rice, C. P. A simple method for the determination of trace levels of alkylphenolic compounds in fish tissue using pressurized fluid extraction, solid phase cleanup, and high-performance liquid chromatography fluorescence detection. *J. Agric. Food Chem.* **2002**, *50* (6), 1350–1354.
- Loyo-Rosales, J. E.; Schmitz-Afonso, I.; Rice, C. P.; Torrents, A. Analysis of octyl- and nonylphenol and their ethoxylates in water and sediments by liquid chromatography/tandem mass spectrometry. *Anal. Chem.* **2003**, *75* (18), 4811–4817.
- Ferguson, P. L.; Iden, C. R.; Brownawell, B. J. Analysis of nonylphenol and nonylphenol ethoxylates in environmental samples by mixed-mode high-performance liquid chromatography-electrospray mass spectrometry. *J. Chromatogr. A* **2001**, *938* (1–2), 79–91.
- Loyo-Rosales, J. E.; Rice, C. P.; Torrents, A. Octyl- and nonylphenol ethoxylates and carboxylates in wastewater and sediments by isotope dilution liquid chromatography/tandem mass spectrometry. *Chemosphere* [Online early access]. doi: 10.1016/j.chemosphere.2007.02.002. Published Online: 2007.
- Bennie, D. T. Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates. *Water Qual. Res. J. Can.* **1999**, *34* (1), 79–122.
- Ying, G.-G.; Williams, B.; Kookana, R. Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. *Environ. Int.* **2002**, *28* (3), 215–226.
- Montgomery-Brown, J.; Reinhard, M. Occurrence and behavior of alkylphenol polyethoxylates in the environment. *Environ. Eng. Sci.* **2003**, *20* (5), 471–486.
- Snedecor, G. W.; Cochran, W. G. *Statistical Methods*, 8th ed; Iowa State University Press: Ames, IA, 1989.
- Fensterheim, R. J. Comment on “Estrogenicity determination in sewage treatment plants and surface waters from the Catalanian area (NE Spain).” *Environ. Sci. Technol.* **2001**, *35* (20), 4156.
- Environment Canada; Health Canada. *Nonylphenol and its Ethoxylates. Priority Substances List Assessment Report, Canadian Environmental Protection Act*; Environment Canada; Health Canada: Quebec, 2001; ISBN 0–662-29248–0.

- (24) Ahel, M.; Giger, W. Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. *Chemosphere* **1993**, 26 (8), 1471–1478.
- (25) Talmage, S. S. *Environmental and human safety of major surfactants. Alcohol ethoxylates and alkylphenol ethoxylates*; The Soap and Detergent Association and Lewis Publishers: Boca Raton, FL, 1994.
- (26) Vivian, C. M. G. Tracers of sewage-sludge in the marine environment—A review. *Sci. Total Environ.* **1986**, 53 (1–2), 5–40.
- (27) McCoy, M. Going green. *Chem. Eng. News* **2007**, 85 (5), 13–19.
- (28) Laundry detergents: Clean & green options. *Consumer Reports*, Jan., 2007, pp 43–44.

Received for review March 22, 2007. Revised manuscript received July 17, 2007. Accepted July 30, 2007.

ES070713I